

Studies on peroxide vulcanization of silica-filled EPDM rubber in presence of vinyl silane coupling agent

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The effect of vinyltris (2-methoxyethoxy) silane (hereafter referred to as A-172) on peroxide-vulcanization, rubber-filler interaction, network structure and fracture mode of EPDM rubber vulcanizate has been studied by chemical analyses and scanning electron microscopy (SEM). A-172 decreases the Mooney viscosity and increases the Mooney scorch time, thus showing improvement in processibility. Rubber-filler interaction and apparent crosslink density increase in the presence of A-172, which is reflected in the technical properties studied. Analyses of fracture surfaces by SEM show the reduction of hydrophilicity of silica filler and its subsequent improved compatibility with hydrophobic hydrocarbon rubber.

(Keywords: rubber; peroxide vulcanization; silica; silane coupling agent; coupling bond; fracture mode)

INTRODUCTION

Several researchers¹⁻⁷ have studied the effect of saturated silane coupling agent on sulphur vulcanization of EPDM rubber filled with siliceous fillers such as silica and clay. Pal and De⁸ have studied the effect of bis(triethoxysilyl propyl) tetrasulphide (hereafter referred to as Si-69) on sulphur vulcanization, polymer-filler interaction, network structure and failure properties of silica- and clay-filled EPDM rubber. However, improved ageing resistance, wet electrical properties and set properties are obtained by peroxide vulcanization. Unsaturated silane coupling agents have been found to be effective in peroxide vulcanization of silica-filled EPDM rubber^{3,4,9-12}. This paper reports the results of investigations on rubber-filler interaction, network structure, technical properties and scanning electron microscopy (SEM) studies on fracture surfaces of silica-filled EPDM rubber vulcanized by dicumyl peroxide (hereafter referred

to as DCP) in absence and in presence of vinyltris-(2-methoxyethoxy) silane.

EXPERIMENTAL

The formulations of the mixes are given in Table 1. Their curing parameters as obtained using the Monsanto rheometer (R-100) and Mooney shearing disk viscometer are shown in Table 2. The mixes were prepared in a conventional laboratory-size rubber mill (32.5 cm × 15 cm). Vulcanization was carried out at 150°C to the respective optimum cure times of the mixes in an electrically heated press. Moldings were cooled in water immediately after the end of the curing cycle¹³.

Determination of rubber-filler interaction

The extent of rubber-filler interaction which causes reinforcement, was determined using the equation of Cun-

Table 1 Formulation of mixes

Ingredients	Mix number								
	A	B	C	D	E	F	G	H	I
Nordel 2722 ^a	100	100	100	100	100	100	100	100	100
Zinc oxide	5	5	5	5	5	5	5	5	5
Vulcasil S ^b	—	5	20	30	40	5	20	30	40
Naphthenic oil	—	0.63	2.50	3.75	5.00	0.63	2.50	3.75	5.00
Di Cup 40C ^c	10	10	10	10	10	10	10	10	10
A-172 ^d	—	—	—	—	—	0.37	1.50	2.25	3.00

^a High ethylene content ethylene-propylene-1,4-hexadiene terpolymer, obtained from Indian Cable Company Limited, Jamshedpur, India

^b Precipitated silica, obtained from Modi Rubber Limited, Modipuram 250110, India

^c 40% dicumyl peroxide on calcium carbonate, obtained from Bengal Waterproof Works Limited, Calcutta

^d Vinyltris (2-methoxyethoxy) silane, obtained from Indian Cable Company Limited, Jamshedpur, India

Table 2 Curing parameters of mixes obtained using Mooney shearing disc viscometer and Monsanto rheometer (R-100)

Parameter	No additive					A-172			
	Silica (%) 0	5	20	30	40	5	20	30	40
	A	B	C	D	E	F	G	H	I
Mooney viscosity, ML (1 + 4), 120°C	30	38	45	69	90	32	36	49	54
Mooney scorch time, at 120°C (min)	22	24	19	18	13	31	31	32	27
Rheometric optimum cure time, at 150°C (min)	27.0	26.0	25.0	23.0	23.0	26.5	26.5	25.0	26.0

neen and Russell¹⁴ (equation (3)), which is derived from the original equation of Lorenz and Parks¹⁵ (equation (1)),

$$\frac{Q_f}{Q_g} = ae^{-Z} + b \quad (1)$$

Also,

$$\frac{Q_f}{Q_g} = \frac{V_{ro}(1 - V_{rf})}{V_{rf}(1 - V_{ro})} \approx \frac{V_{ro}}{V_{rf}} \quad (2)$$

So,

$$\frac{V_{ro}}{V_{rf}} = ae^{-Z} + b \quad (3)$$

where Q is the amount of solvent imbibed per unit weight of the rubber; f and g refer to filled and gum mixes; V_{ro} and V_{rf} are the volume fractions of rubber in unfilled and filled vulcanizates, respectively, swollen in a solvent. Z is the weight fraction of filler in the vulcanizate, and a and b are constants characteristic of the system. By plotting V_{ro}/V_{rf} versus e^{-Z} , values of a (slope) and b (intercept) were determined. As the value of a increases the swelling restriction and reinforcement increases also¹⁶⁻¹⁸.

The degree of reinforcement was also studied by using the equation of Kraus¹⁹:

$$\frac{V_{ro}}{V_{rf}} = 1 - m\theta/(1 - \theta) \quad (4)$$

where

$$m = 3c(1 - V_{ro}^{1/3}) + V_{ro} - 1 \quad (5)$$

Here θ is the volume fraction of filler in the filled vulcanizate and c is a constant characteristic of the filler, but independent of the polymer, the solvent or the degree of vulcanization. The slope of the curve obtained by plotting V_{ro}/V_{rf} versus $\theta/(1 - \theta)$ provides an indication of the degree of reinforcement for the larger the slope, the greater the reinforcement. Rubber-filler attachment, defined here as the 'apparent coupling bond', was determined from the difference of 'apparent' chemical crosslink density (derived using the equation of Parks and Brown²⁰, (equation (6))) before and after treatment of ammonia-modified swelling of the vulcanizates^{21,22}.

Determination of network structure and technical properties

Volume fraction of rubber (V_r) in the vulcanizates swollen in a solvent and the technical properties were determined according to ASTM methods and were the same as adopted in previous studies^{13,23}.

The 'apparent' chemical crosslink density was determined¹⁶ by swelling of a weighed sample of vulcanizate in benzene till the equilibrium swelling was attained, which was 8 h in this case. The swelling value, Q , defined as the weight of benzene (g) per unit weight of rubber

hydrocarbon (g), was calculated from the equation of Parks and Brown²⁰ (equation (6)) as follows:

$$Q = \frac{(\text{Swollen weight} - \text{dried weight})}{\left(\frac{\text{Original weight} \times 100}{\text{formula weight}} \right)} \quad (6)$$

where the formula weight is the total weight of rubber plus compounding ingredients based on 100 parts of rubber. A comparison of the cross-linking was then made from the reciprocal swelling value, $1/Q$.

Ammonia-modified swelling

Rubber-filler attachment (or apparent coupling bond) was determined by the chemical cleavage of rubber-filler bonds by swelling the vulcanizate samples for 48 h in benzene in an ammonia atmosphere^{21,22}. Details of the procedure are given elsewhere^{17,18}. The differences in apparent cross-linking of the original vulcanizates and the same after ammonia treatment gives a measure of the amount of rubber-filler attachment (or apparent coupling bond).

Scanning electron microscopy studies

Figure 1 shows the direction in which force was applied in tensile and tear tests. Figure 2 indicates the direction of bend flexing. After the completion of tensile, tear and bend flexing tests, the fracture surfaces were carefully cut from one of the two pieces of the failed test specimens without touching the surfaces.

The fractured test specimens were stored in a desiccator to avoid contamination and then sputter-coated with gold within 24 h of testing. SEM photographs of the gold coated surfaces were taken within 48 h of testing, using a Phillips 500 model scanning electron microscope at 0° tilt. The respective scan areas of the specimens are also shown in Figures 1 and 2.

It has been found from preliminary studies that storage of fractured specimens in a desiccator up to a period of one week before gold coating and up to a period of one month after gold coating, does not alter the fracture surface topography as observed in the SEM.

RESULTS AND DISCUSSION

Viscosity, scorch and cure time

Mooney viscosity of the mixes are lowered substantially by the presence of A-172, which reduces the hydrophilicity of the hydrated silica by providing a more hydrophobic, hydrocarbon-compatible surface by the reaction of its alkoxy groups with the silanol groups (-SiOH) of silica. This hydrophobation reaction causes the cleavage of secondary agglomeration of fillers (pri-

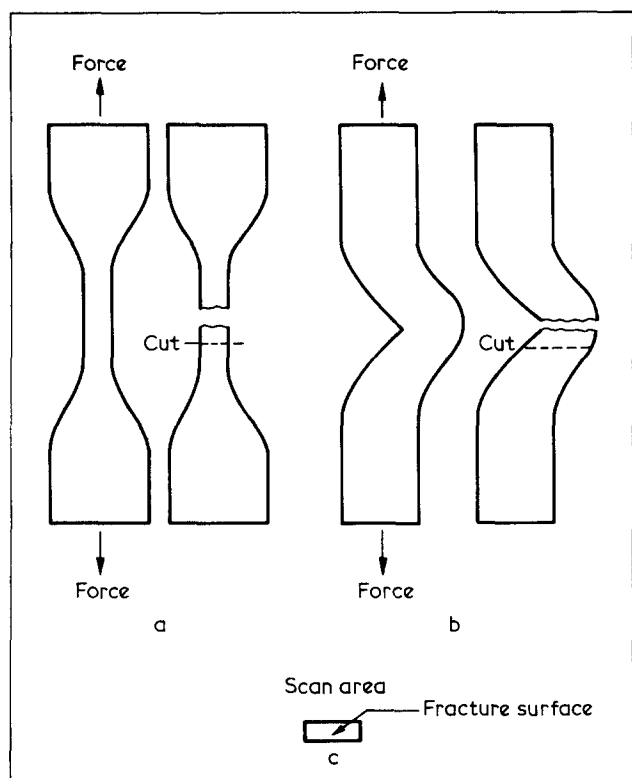


Figure 1 (a) Tensile test specimen before and after testing; (b) tear test specimen before and after testing; and (c) fracture surface, cut from the failed test pieces

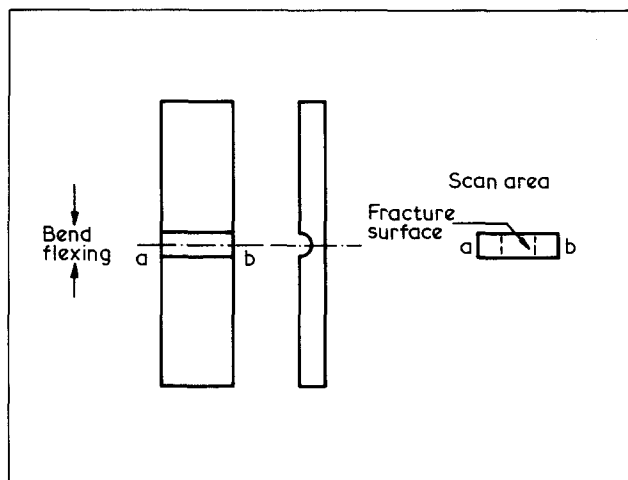


Figure 2 Mode of failure after bend flexing and scan area of fracture surface.

marily hydrogen bonds), responsible for the unusual high viscosity of the silica filled mixes without coupling agent²⁴.

A-172 increases the Mooney scorch time, whereas optimum cure time remains almost unaffected in the presence of A-172. Vondracek *et al.*¹¹ and Comen *et al.*²⁵ also found that A-172 did not affect the cure rate properties of peroxide cured EPDM rubber.

Rubber-filler interaction

To evaluate the rubber-filler interaction, the values of V_{ro}/V_{rf} are plotted versus e^{-z} (Figure 3).

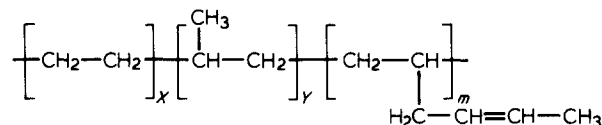
It is evident from Figure 3 that in the absence of A-172, as the filler loading increases (higher filler loading meaning lower value of e^{-z}), values of V_{ro}/V_{rf} increase to > 1 .

This indicates that the formation of vacuoles and rubber-filler detachments at the rubber-filler interface is increasing due to un wetting of the filler by the rubber matrix. However, in the presence of A-172, the trend is the opposite. With the increase of silica loading, V_{ro}/V_{rf} values decrease showing enhanced rubber-filler interaction. It is also apparent that reinforcement is more prominent at higher filler loading.

Analysis of Kraus plots¹⁹, as shown in Figure 4, also reveals the similar phenomenon of rubber-filler interaction in the presence of A-172.

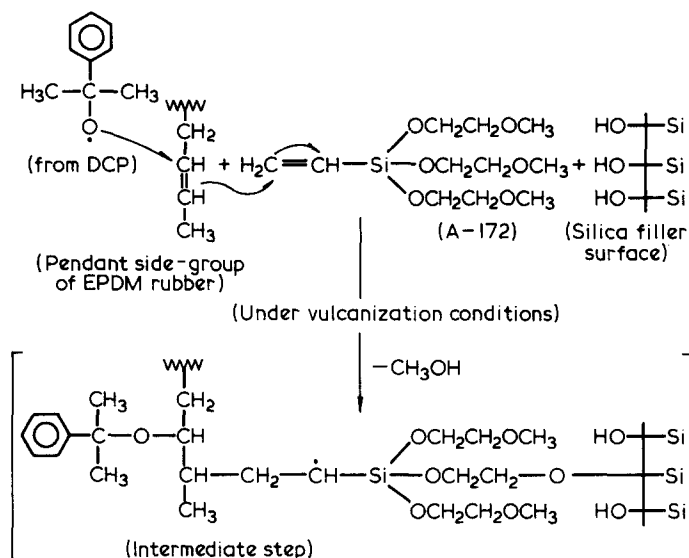
A mechanism of rubber-filler interaction or reinforcement due to the incorporation of A-172 in silica-filled EPDM rubber vulcanized by DCP is proposed as follows.

The molecular structure of the EPDM rubber studied here can be represented as:



where X, Y and m are integers, and $m < X$ and Y.

The unsaturation in the EPDM rubber is located in a pendant side group and not in the polymer backbone itself. So, unlike natural rubber^{17,18} and other unsaturated elastomers⁴ which contain unsaturation at the polymer backbone, the interaction between the rubber and the surface silanol groups (-SiOH) of silica takes place at the pendant olefinic unit of the rubber through the coupling agent (A-172):



According to this reaction mechanism, it is found that a single molecule of A-172 can couple free radically with each olefinic unit of the pendant side-group of EPDM rubber, and also with one unit of silica through condensation of its alkoxy groups and surface -OH groups of silica resulting in the formation of ether linkages. Here the cumyloxy radical derived from dicumyl peroxide facilitates the creation of a free radical on the sp^2 -carbon which may undergo interaction with the vinyl group of A-172. The product thus formed having a free radical on methene carbon may continue further coupling reactions.

The increased rubber-filler interaction in the presence of A-172 can thus be understood.

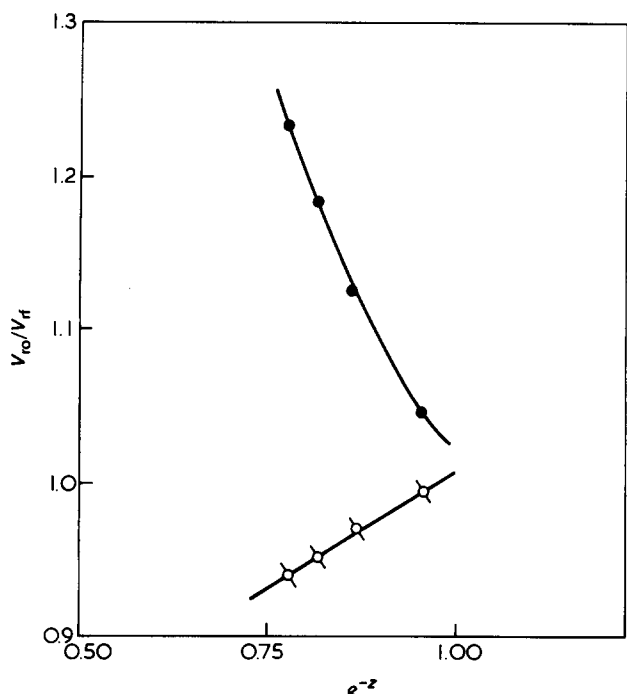


Figure 3 Plot of V_{ro}/V_{rf} against e^{-Z} . \circ , With A-172; \bullet , without A-172

Network structure and technical properties

The volume fraction of rubber (V_r) and the apparent cross-link density ($1/Q$) of the respective mixes are shown in Table 3.

It is evident from Table 3 that in the absence of A-172, addition of silica decreases both V_r and $1/Q$. This appears to be due to the unwetting of hydrophilic silica with the hydrophobic rubber, resulting in detachment at the rubber-filler interface. However, in the presence of A-172, increased addition of silica gradually increases the V_r and $1/Q$ values due to enhanced rubber-filler attachment. This is due to the fact that A-172 reduces the hydrophilic character of silica surface, making it more compatible with the hydrophobic EPDM rubber.

The chemical interaction between filler surface and the rubber in presence of A-172 has been discussed previously.

Technical properties of the vulcanizates, as shown in Table 4, show that at all levels of filler loading, A-172 improves almost all the physical properties, i.e. the modulus, rebound resilience, hardness, compression set, resistance to abrasion, Goodrich heat build-up and dynamic set except tensile and tear strength. As A-172 increases both the apparent cross-link density (Table 3) and apparent coupling bond (Figure 5), higher values of modulus and hardness and lower values of set and heat build-up are expected. Ulmer *et al.*²⁶ have shown that heat build-up is directly proportional to the viscous

modulus of rubber and the viscous modulus in turn is inversely related to total amount of chemical cross-links and coupling bonds. Increase in rubber-filler attachment in the presence of A-172 appears to increase the abrasion resistance also. Wagner^{27,28} and Dannenberg²⁹ also found similar phenomenon.

At lower filler loadings, tensile strength and resistance to tearing increase in the presence of A-172 but at higher filler loadings, A-172 appears to have an adverse effect. Edwards³⁰ noted that network structure and coupling bonds must be properly balanced to attain maximum tensile strength, and rubber-filler bonds are not a 'necessary condition' for reinforcement.

It is evident from Figures 3-5 that the rubber-filler attachment or adhesion increases sharply at larger filler loading. Erickson³¹ showed that a high density of interfacial bonding would be detrimental by making the interface brittle and weak. The higher proportion of coupling bond appears to interfere with the molecular alignment, stress redistribution and strain-energy dissipation in the network under stress, resulting in low tensile and tear strength values. This observation is consistent with the slippage mechanism³².

It is evident from Table 4 that ageing properties are not influenced by the presence of A-172.

To understand the failure mechanism, the fracture surfaces of gum (unfilled) and filled vulcanizates at 40% silica level were examined using SEM. SEM fractographs have been found to depend on the type of failure test

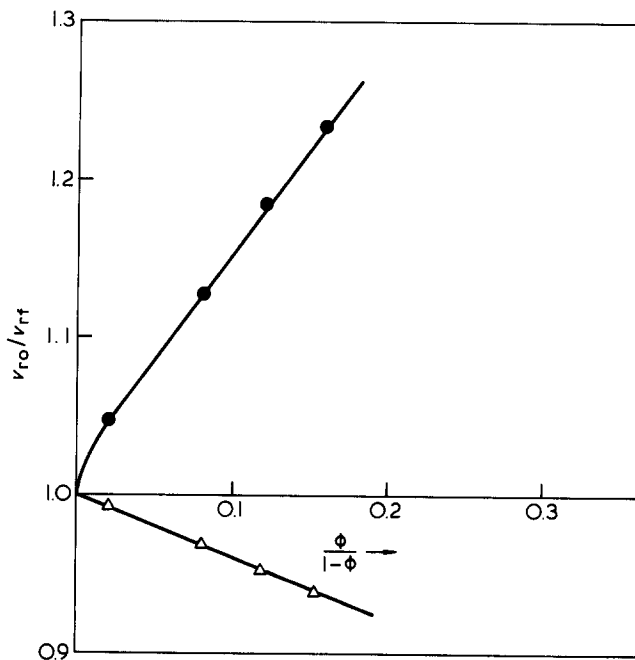


Figure 4 Plot of V_{ro}/V_{rf} against $\phi/(1-\phi)$. \triangle , With A-172; \bullet , without A-172

Table 3 Chemical characterization of vulcanizates

Parameter	No additive					A-172			
	Silica (%) 0		20	30	40	5	20	30	40
	A	B	C	D	E	F	G	H	I
Volume fraction of rubber, V_r	0.415	0.396	0.369	0.350	0.336	0.417	0.428	0.436	0.442
Apparent cross-link density, $1/Q$	0.681	0.644	0.580	0.539	0.514	0.684	0.712	0.740	0.769

Table 4 Physical properties of vulcanizates^a

Property	No additive					A-172			
	Silica (%) 0	5	20	30	40	5	20	30	40
	A	B	C	D	E	F	G	H	I
Tensile strength (MPa)	3.4 (82)	4.5 (82)	7.8 (77)	10.2 (78)	18.1 (73)	6.2 (79)	10.1 (85)	12.3 (80)	16.2 (76)
Modulus 300% (MPa)	<i>b</i>	4.2 (-)	5.6 (-)	7.0 (-)	8.3 (148)	5.8 (-)	9.7 (-)	<i>b</i>	<i>b</i>
Elongation at break (%)	260 (88)	310 (83)	330 (78)	360 (78)	450 (69)	310 (90)	335 (86)	250 (88)	230 (93)
Tear strength (kN m ⁻¹)	9.3 (69)	12.1 (84)	20.3 (95)	25.7 (91)	39.1 (94)	16.9 (85)	24.7 (88)	27.3 (93)	33.8 (90)
Hardness, shore A	80 (98)	81 (99)	85 (102)	88 (102)	91 (103)	82 (99)	87 (100)	90 (101)	93 (101)
Rebound resilience (%)	62	60	54	49	43	60	57	52	47
Compression set (%)	1	4	8	11	19	2	5	8	12
Flex cracking resistance (kilocycles)	0.1	0.1	0.1	0.3	2.5	0.1	0.2	0.5	1.6
Abrasion loss (cm ³ h ⁻¹)	1.8	1.2	1.1	0.9	0.8	1.0	0.7	0.6	0.4
Heat build-up (ΔT°C)	10	13	21	28	38	11	16	21	27
Dynamic set (%)	0.8	1.6	3.1	4.3	7.6	1.2	1.6	2.2	3.6

^a Values in parentheses are per cent retained of the respective properties after ageing at 100°C for 4 days

^b Modulus at 300% was not obtained

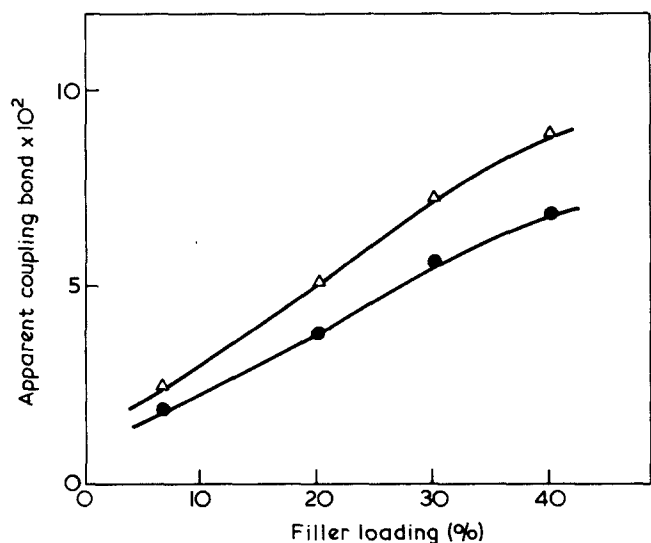


Figure 5 Variation of apparent coupling bond with filler loading. Δ , With A-172; \bullet , without A-172

(tensile/tear/flexing/abrasion) and on the nature of vulcanizate (gum/filled)³⁴⁻⁴⁰.

Figure 6 is a tensile fractograph of gum EPDM vulcanizate (mix A) and shows the network of parallel channel-type cracks on the smooth surface indicating poor tensile strength. Addition of 40% silica (mix E) increases the strength and changes the fracture topography. Unwetting of the filler by the rubber matrix and pulling out of the filler aggregates under stress is evident from the fractograph (Figure 7). The network of cracks is dominated by the roughness of the surface and several tear paths. Incorporation of A-172 (mix I) does not cause much change in surface topography, but the network of cracks is visible (Figure 8). Mix I gives lower tensile strength than the corresponding control vulcanizate of mix E.

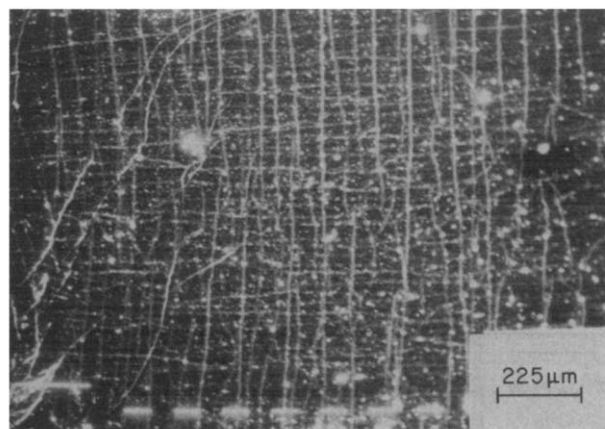


Figure 6 SEM micrograph of tensile fracture surface. Surface showing network of parallel channel-type cracks of mix A

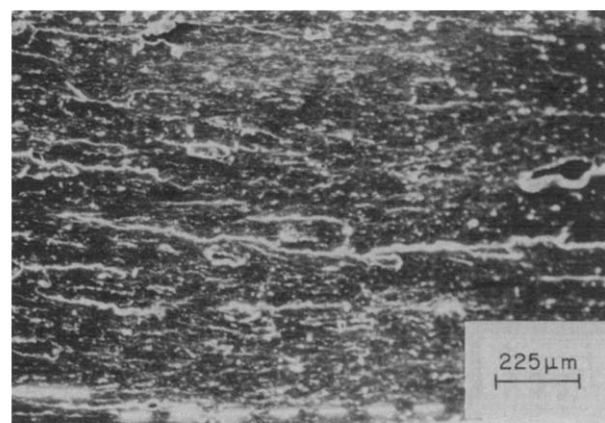


Figure 7 SEM micrograph of tensile fracture surface. Rough surface containing tear paths and debonded filler of mix E

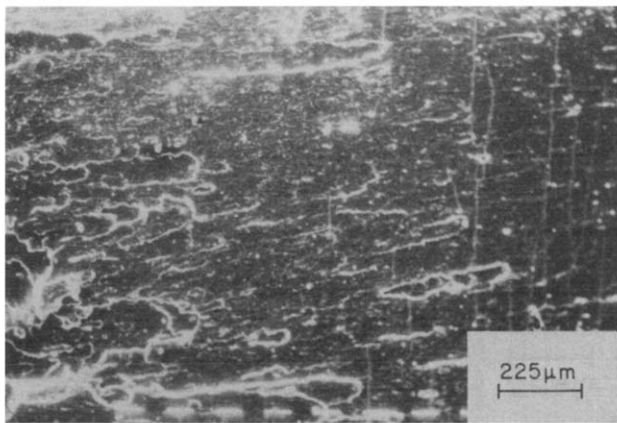


Figure 8 SEM micrograph of tensile fracture surface. Network of cracks on the rough surface of mix I

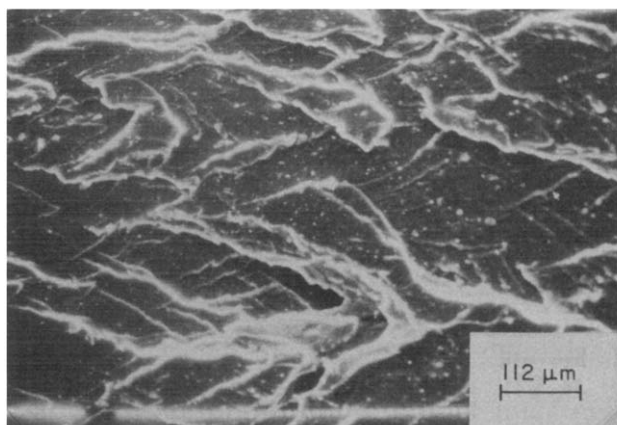


Figure 9 SEM micrograph of tear fracture surface. Branched and interconnected tear lines of mix A

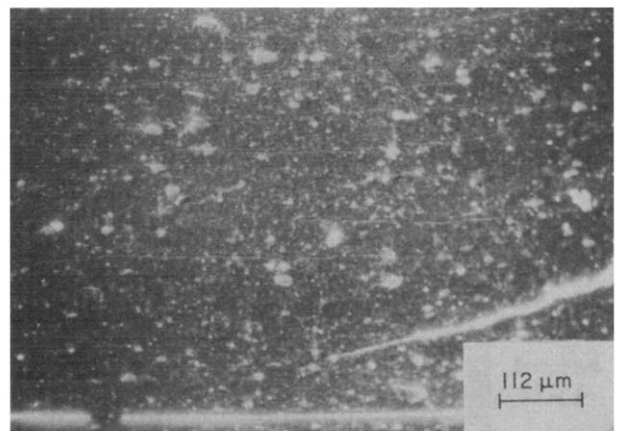


Figure 10 SEM micrograph of tear fracture surface. Smooth surface containing few crack paths of mix E

Figure 9 is the tear fractograph of gum EPDM vulcanizate (mix A) and shows a large number of tear lines consisting of branches, interconnected lines and fracture in different planes. Mix A shows very poor tear strength. Tear fractograph of mix E (40% silica without A-172) shows smooth surface (Figure 10) and unwetting and pulling out of the filler under stress on the surface which contains a few crack paths (Figure 11). Tear fractograph of mix I (40% silica with A-172) shows a smooth surface with small tear-lines (Figure 12) containing a distinct tear ridge

(Figure 13). Expectedly, mix I has lower tear strength than mix E. Dreyfuss, Gent and William³³ also have found that the tear strength does not appear to depend upon the degree of interfacial bonding to a significant degree.

In the case of flex fatigue properties, unlike natural rubber which is strain-induced crystallized rubber, the gum (unfilled) vulcanizates of which provide more flexing resistance than that of filled vulcanizates^{17,34}, EPDM gum vulcanizate (mix A) shows poor flexing resistance. Flex fractographs (Figures 14 and 15) of mix A show brittle and cleavage fracture. Figures 16 and 17 are the flex

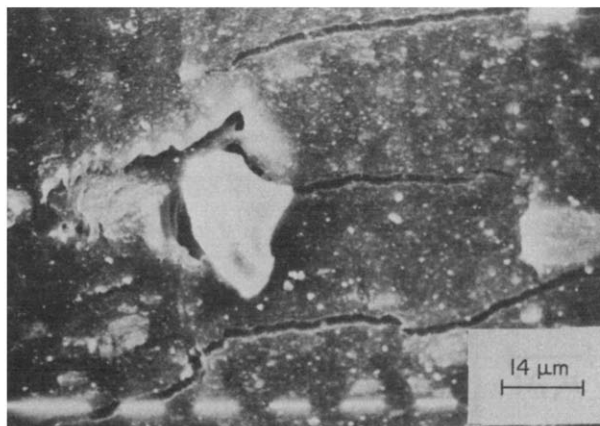


Figure 11 SEM micrograph of tear fracture surface. Pulling out of the filler and crack paths on the surface of mix E

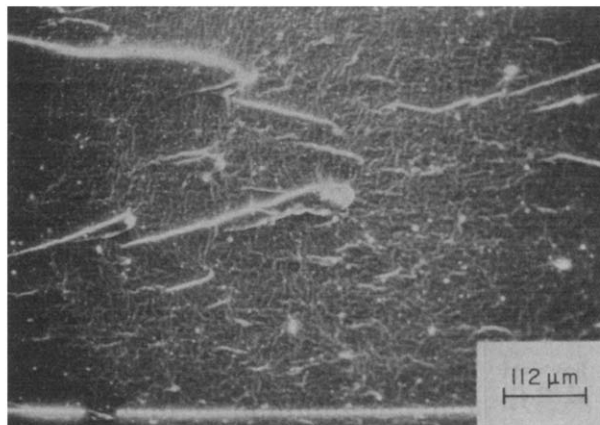


Figure 12 SEM micrograph of tear fracture surface. Surface containing small tear lines of mix I

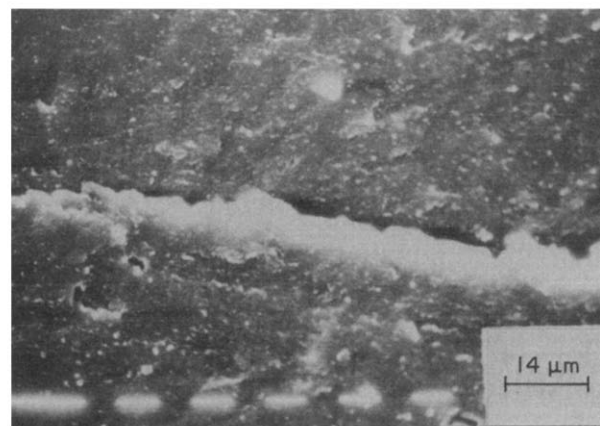


Figure 13 SEM micrograph of tear fracture surface. A distinct tear ridge on the surface of mix I

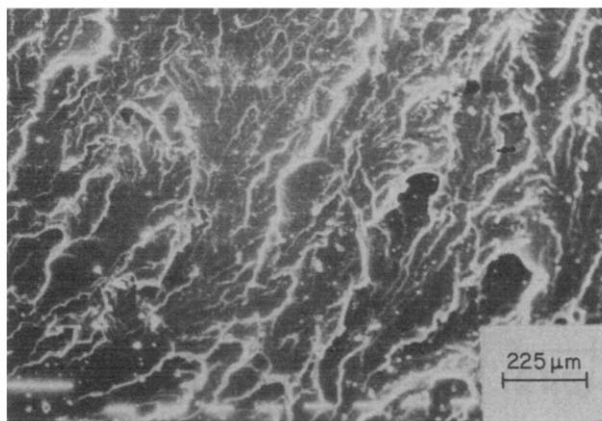


Figure 14 SEM micrograph of flex fracture surface. Brittle fracture of mix A

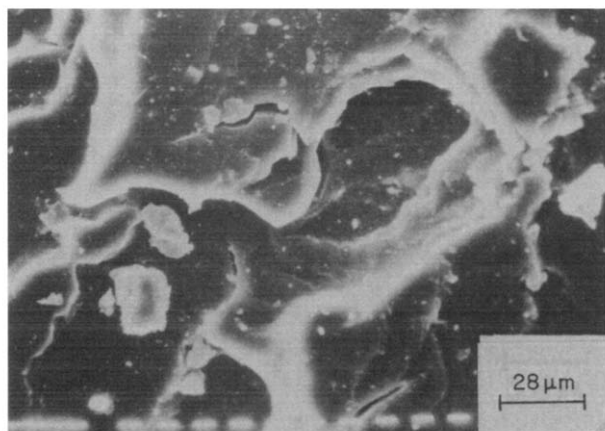


Figure 15 SEM micrograph of flex fracture surface. Surface showing cleavage fracture of mix A

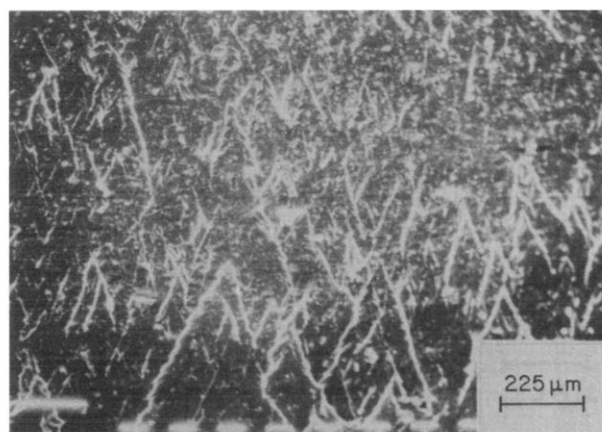


Figure 16 SEM micrograph of flex fracture surface. Fatigue striations of mix E

fractographs of mix E (40% silica, without A-172) which show distinct fatigue striations. Figures 18 and 19 are the flex fractographs of mix I (40% silica, with A-172). Fatigue striations are more prominent, even at lower magnification. Flex resistance of mix I is marginally lower than mix E.

A comparison of the fractographs of silica-filled sulphur vulcanized EPDM rubber⁸ and silica-filled peroxide vulcanized EPDM rubber (present work) shows that the fractographs are similar in both cases. This shows that

basic mechanism of failure of silica-filled EPDM rubber is independent of the nature of the coupling agent-vulcanizing system combination.

CONCLUSIONS

(1) Vinylsilane coupling agent (A-172) decreases the Mooney viscosity and increases the scorch time of silica-filled EPDM. Optimum cure time, however, remains almost unchanged on addition of A-172.

(2) A-172 increases both apparent cross-link density and apparent coupling bond.

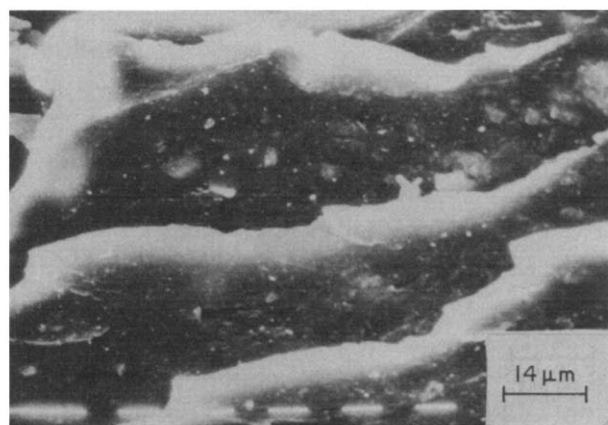


Figure 17 SEM micrograph of flex fracture surface. Distinct fatigue striations of mix E at higher magnification

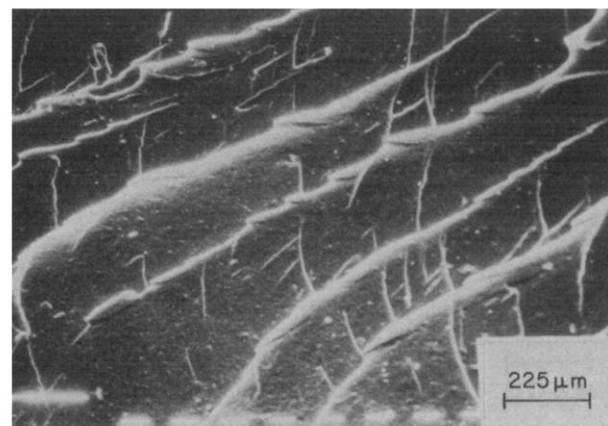


Figure 18 SEM micrograph of flex fracture surface. General surface showing fatigue striations of mix I

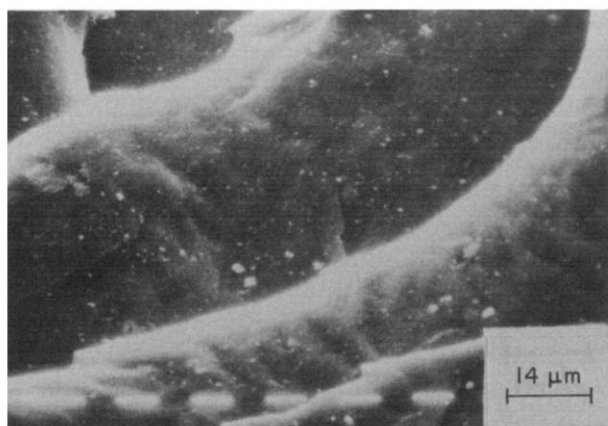


Figure 19 SEM micrograph of flex fracture surface. Fatigue striations on the surface of mix I at higher magnification

(3) A-172 improves both static properties and dynamic properties. At higher filler loading, however, A-172 causes reduction in tensile, tear and flex resistance.

(4) Ageing properties are not influenced by the presence of A-172.

(5) SEM studies of fractured surfaces under tension, tear and flexing have been carried out, and changes in strength of the vulcanizates have been correlated with fractographs.

REFERENCES

- 1 Burg, G. R. 108th meeting Am. Chem. Soc., Rubber Div., New Orleans, La., Oct. 7-10, 1975
- 2 MacDonald, G. W. *Rubber Age* 1970, **102**, 66
- 3 Ranney, M. W. and Pagano, C. A. *Rubber Chem. Technol.* 1971, **44**, 1080
- 4 Ranney, M. W., Sollman, K. J. and Pickwell, R. J. 100th meeting Am. Chem. Soc., Rubber Div., Cleveland, Ohio, Oct. 12-15, 1971
- 5 Libby, P. W., Iannicelli, J. and McGill, C. R. 91st meeting Am. Chem. Soc., Rubber Div., Montreal, May 2-5, 1967
- 6 Wolff, S. 'Si-69 in EPDM' Degussa Information Bulletin for the Rubber Industry, Degussa Pigments Division, Federal Republic of Germany, p. 1139
- 7 Ranney, M. W., Sollman, K. and Cameron, G. Int. Rubber Conf., DKG, Munich, Sept. 2-5, 1974
- 8 Pal, P. K. and De, S. K. *Rubber Chem. Technol.* 1983, **56**, 737
- 9 Blodgett, R. B. *Rubber Chem. Technol.* 1979, **52**, 410
- 10 Wagner, M. P. *Rubber Chem. Technol.* 1974, **47**, 697
- 11 Vondracek, P., Capka, M. and Schatz, M. *J. Appl. Polym. Sci.* 1979, **24**, 1619
- 12 Vondracek, P. and Schatz, M. *Elektroizolacna Kablova Tech.* 1979, **32**, 17
- 13 Mukhopadhyay, R., De, S. K. and Chakraborty, S. N. *Polymer* 1977, **18**, 1243
- 14 Cunneen, J. I. and Russell, R. M. *Rubber Chem. Technol.* 1970, **43**, 1215
- 15 Lorenz, O. and Parks, C. R. *J. Polym. Sci.* 1961, **50**, 299
- 16 Mukhopadhyay, R. and De, S. K. *Rubber Chem. Technol.* 1979, **52**, 263
- 17 Pal, P. K. and De, S. K. *Rubber Chem. Technol.* 1982, **55**, 1370
- 18 Pal, Pranab K., Chakravarty, S. N. and De, S. K. *J. Appl. Polym. Sci.* 1983, **28**, 659
- 19 Kraus, G. J. *J. Appl. Polym. Sci.* 1963, **7**, 861; also *Rubber Chem. Technol.* 1964, **37**, 6
- 20 Parks, C. R. and Brown, R. J. *Rubber Chem. Technol.* 1976, **49**, 233
- 21 Polmanteer, K. E. and Lentz, C. W. *Rubber Chem. Technol.* 1975, **48**, 795
- 22 Vondracek, P. and Schatz, M. *J. Appl. Polym. Sci.* 1979, **23**, 2681
- 23 Pal, P. K., Bhowmick, A. K. and De, S. K. *Rubber Chem. Technol.* 1982, **55**, 23
- 24 Wolff, S. 116th meeting Am. Chem. Soc., Rubber Div., Cleveland, Ohio, Oct. 23-26, 1979
- 25 Comen, A. L. and Body, R. W. 114th meeting Am. Chem. Soc., Rubber Div., Boston, Massachusetts, Oct. 10-13, 1978
- 26 Ulmer, J. D., Chirico, V. E. and Scott, C. E. *Rubber Chem. Technol.* 1973, **46**, 897
- 27 Wagner, M. P. *Rubber World* 1971, **164**(5), 46
- 28 Wagner, M. P. *Colloq. Int. C.N.R.S.* 1975, **213**, 147
- 29 Dannenberg, E. M. *Rubber Chem. Technol.* 1975, **48**, 410
- 30 Edwards, D. C. and Fischer, E. *Kautsch. Gummi Kunstst.* 1973, **26**(2), 46
- 31 Erickson, P. W. *J. Adhes.* 1970, **2**, 184
- 32 Dannenberg, E. M. *Trans. Inst. Rubber Ind.* 1966, **42**, T 26
- 33 Dreyfuss, P., Gent, A. N. and Williams, J. R. *J. Polym. Sci., Polym. Phys. Edn.* 1980, **18**, 2135
- 34 Pal, P. K., Bhowmick, A. K. and De, S. K. *Int. J. Polym. Mat.* 1982, **9**, 139
- 35 Mathew, N. M. and De, S. K. *Polymer* 1982, **23**, 632
- 36 Mathew, N. M., Bhowmick, A. K. and De, S. K. *Rubber Chem. Technol.* 1982, **55**, 51
- 37 Mathew, N. M., Bhowmick, A. K., Dhindaw, B. K. and De, S. K. *J. Mater. Sci.* 1982, **17**, 2554
- 38 Chakraborty, S. K., Bhowmick, A. K., De, S. K. and Dhindaw, B. K. *Rubber Chem. Technol.* 1982, **55**, 41
- 39 Setua, D. K. and De, S. K. *J. Mater. Sci.* in press
- 40 Mathew, N. M. and De, S. K. *J. Mater. Sci.* 1983, **18**, 515